From,

Mrs.Sneha B S
Research scholar(Part –time)
Department of Chemistry
Mangalore University, Mangalagangothri-574199

To,

The registrar (Evaluation)
Mangalore University, Mangalagangothri-574199

Through,

1. Professor. B. Narayana
   Research Guide
   Department of Chemistry
   Mangalore University
   Mangalagangothri-574199

2. The Chairman
   Department of Chemistry
   Mangalore University
   Mangalagangothri-574199

Respected Sir,

Sub: Submission of final -synopsis reg.
Ref: MU/EXB/Ph. D./CR-05/Chem./2018-19/E.13 dated 28-05-2018

Inviting reference to the above, I am submitting herewith 12 copies of final synopsis of my Ph.D. thesis work entitled "Study of Adsorption Process Using Plant Based Activated Carbons' for the degree of Doctor of Philosophy in Chemistry. So, I kindly request you to do the needful and oblige.

Thanking you, Yours faithfully,

(**Sneha B S**)

Forwarded with the recommendation to the Chairman, Department of Chemistry, Mangalore University for onward transmission to the Registrar (Evaluation), Mangalore University.

Date: **Professor. B. Narayana**
Place: Mangalagangothri (Research Guide)

SYNOPSIS

STUDY OF ADSORPTION USING PLANT-BASED ACTIVATED CARBONS

Introduction

In the industry, activated carbon is primarily employed for the adsorption of non-essential species from different liquid and gas phase adsorptions. Food processing, the manufacture of alcoholic beverages, the decolorization of oils and fats, product purification in sugar refining, gold recovery, and the refinement of liquid fuels are all applications for the liquid phase. Additionally, it is used in processes for purification such as electroplating, chemical purification, textile, personal care, and cosmetics industries, as well as chemical and petrochemical industries [1,2]. Applications for organic solvent recovery in the gas phase; purification of biogas, removal of hazardous components from exhaust fumes, and usage in gas masks, among other things. Additionally, activated carbon is employed in nuclear and vacuum technologies, soil enhancement, pesticide residue removal, and medical and veterinary applications. Furthermore, there are various ecological applications for activated carbon [3]. Activated carbon can also be used for the adsorption of dyes as well as acids.

Recent studies reported that over 15% of the total quantity of dyes produced annually are lost during the production processes and reach industrial wastewater, becoming contaminants of the environment. These dyes show toxic and carcinogenic effects [4, 5], the presence of dyes in the aquatic environment causes the water colouring and limits the oxygenation of water surfaces, significantly affecting aquatic plants and fauna [6, 7]. Most synthetic dyes used in industrial activities are of low cost and high chemical stability [8, 9], which contains aromatic rings in their structure it takes long time for the degradation in environment. Also, these dyes can generate secondary toxic products during degradation, which are harmful to the environment [10].

Various techniques are used for the removal of dyes .Out of which adsorption is generally preferred best technique for the removal of dyes. It is due to adsorption is one of the most

effective, technically-simple, easy to operate and cost-effective wastewater treatment technique [11]. During recent years a number of adsorbents based on the natural wastes such as fruit, husk, leaves, peels, sawdust, barks, nut shells, seeds, bark of trees, hen feathers, and other similar inexpensive materials released from environment are used for the study of adsorption. Among these, leaf-based materials (raw or activated forms) have received increased attention, mainly because they are cheap, available in large quantities in almost all regions of the world, required only a few stages of preparation, and in many cases not have another use [12]. On the other hand, the leaf-based materials of different trees contain a variety of inorganic and organic compounds, such as cellulose, hemicelluloses, pectin, and lignin etc, [13]. These compounds have in their composition various functional groups, such as hydroxyl, carboxyl, carbonyl, amino, and nitro groups [14], which may be responsible for the process adsorption. The present investigation entitled 'Study of adsorption using plant-based activated carbons' has been discussed in six chapters. A short description of the details of the contents in each chapter is described below.

Chapter I

This is an introductory chapter that deals with a brief introduction to the work including the concept of activated charcoal and its adsorption property along with a literature review. The chapter begins with a general introduction to the topic, of carbon and carbon materials. Further, the chapter consists of different sections which describe various aspects related to the preparation and characterization techniques of activated charcoal, applications of activated charcoal in different fields, etc. The chapter also includes a brief detail on the process of adsorption, low-cost activated charcoal used for the adsorption of toxic materials, etc.

Chapter 2

Chapter 2 deals with the materials, methods, and various analytical techniques used throughout this research work. It also describes the chemical reagents used and the methodologies adopted during the study. Materials include i) the precursor used for the preparation of activated charcoal, i.e., agricultural waste materials, ii) the methodology includes the method of preparation and characterization iii) the application of synthesized activated charcoal for the adsorption of malachite green(MG) and oxalic acid(OA). A brief description of the study of adsorption isotherm, kinetics, and thermodynamics of adsorption of MG and OA on synthesized carbons are also included in this chapter.

Preparation of Activated Carbon

The selected raw samples (leaves) were cleaned, washed with water to remove dirt, and later dried in the oven at 130^0C for an hour to remove the moisture content in the sample. The different leaves were crushed into powder and later used for the preparation of the activated carbon.

Three different methods have been adapted for the preparation of activated carbon, namely physical activation method, chemical activation method and microwave activation method.

Physical activation method

For the preparation of physical activated carbon, finely powdered samples were carbonized by using oven and activated by muffle furnace. All the three raw samples such as macaranga indica leaf powder (MI), java apple leaf powder (JA) and cocoa leaf powder (CL) were carbonized at 400˚C for an hour. The obtained activated carbon was ground well by using mortar and stored in air-tight bottle.

Chemical activation

The dried raw materials (MI, JA and CL) were impregnated with 1M $ZnCl_2$ solution and heated on a hot plate for an hour. Then the impregnated raw materials were allowed to remain in contact with the 10% aqueous $ZnCl_2$ solution for 24 hrs. The $ZnCl_2$ solution was removed off and dried in an oven. The impregnated raw materials were subjected to carbonization and activation in the muffle furnace for 1 hour. The obtained carbon was washed with plenty of distilled water to remove excess $ZnCl_2$ which was then tested by silver nitrate test for the presence of chloride ion. The washing was continued till no more chloride ion is left in the filtrate solution. The activated charcoal thus obtained was dried in the oven and ground well using mortar to obtain powdered activated carbon.

Microwave activation method

Regular household microwave oven has been used to prepare microwave activated carbon. The dried sample (leaves) was subjected to microwave treatment (90 W of power) for 2 hours for the MI leaves, 90minutes for JA leaves and 1 hour for CL. These microwave treated samples were then collected, crushed and sieved to required particle size and are used for adsorption studies.

Characterization techniques

The physical and chemical properties of synthesized activated carbons and surface morphology were studied by various techniques. The different techniques are discussed below.

Fourier Transform Infrared Spectroscopy (FTIR)

One of the techniques widely used to identify functional groups in both pure and mixture of compounds is FTIR Spectroscopy.

From FTIR, the various surface functional groups present on the activated carbon are identified. The IR spectrum of the raw samples and prepared carbon were recorded using Fourier Transform Infrared Spectrometer, Shimadzu (Japan) in the wave number range 400-4000 cm^{-1}. During the process the samples were finely ground with potassium bromide pellets under a hydraulic pressure of 600kg/cm^2 and then spectra were recorded.

Powder X-Ray Diffraction

The powder X-ray diffraction method offers qualitative and quantitative data regarding the nature of the substance present in the sample in terms of crystallinity. Powder diffraction has been extensively used for phase identification, particle size analysis, quantitative study of mixture phases, and characterization of physical flaws. It is also used to determine the type and size of the activated carbon that has been manufactured. Materials of very small crystallite size do not give normal diffraction patterns because they lack a sufficient degree of order.

Thermal Analysis

Thermogravimetry (TG) is a method that measures the weight of a substance as a function of time or temperature in either a controlled-rate heated or cooled environment. Thermogravimetry (TG) examines how a material's weight changes when its temperature changes. It establishes the temperature at which the substance begins to lose weight.

Field-Emission Scanning Electron Microscopic Analysis

The scanning electron microscope is very essential in the analysis of the microstructural features of solid objects. FE-SEM offers high-resolution data on the topography (surface aspects of an object), morphology (particle shape and size), and composition (the elements that make up the object) of solid surfaces.

Ultraviolet-Visible Absorption Spectrophotometer

The most common uses of UV-Visible Spectroscopy (Electronic Spectroscopy) are for quantitative analysis and structural elucidation. The UV visible spectrum has a wavelength of 800-200 nm and enough energy to excite valence electrons in atoms or molecules.

The complete chapter can be described in Figure 1. This figure gives the flow chart of the synthesis and characterization of activated carbon.

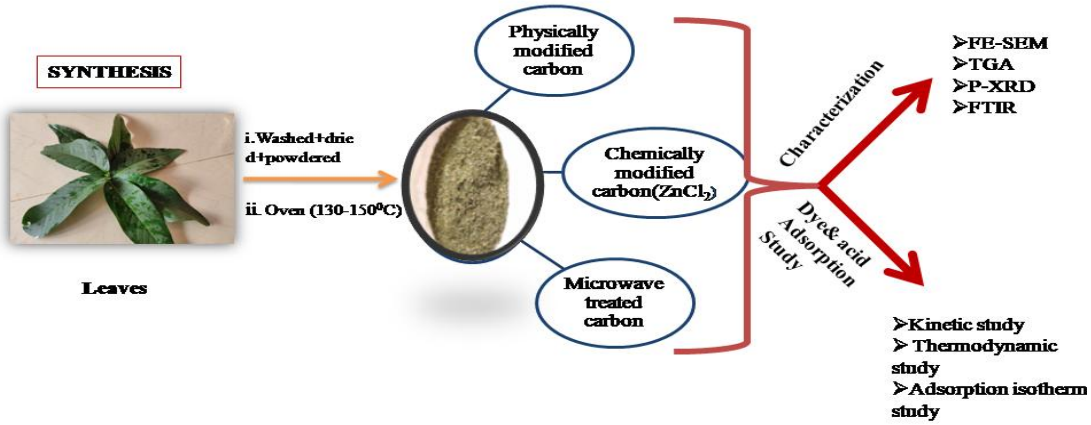

Fig 1: Flow chart of synthesis and characterization of activated carbons

Chapter 3

Chapter 3 discusses the preparation and characterization of activated carbon from Macaranga indica (MI) leaves and its adsorption properties towards Malachite green and oxalic Acid. Activated carbon was prepared from fallen MI leaves by three methods, namely physical, chemical, and microwave activation, and characterized by Powder X-ray diffraction (P-XRD), Scanning Electron Microscopy (FE-SEM), Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetric analysis (TGA). The synthesized carbons were further used as adsorbents for the adsorption of Malachite green and oxalic acid. The present chapter also includes a discussion on the effect of initial dye/acid concentration, contact time, and temperature on the adsorption process. Based on the data, adsorption isotherm, kinetics, and thermodynamics of adsorption were evaluated.

Chapter 3A

It describes the adsorption study of various activated charcoals on cationic dye, MG. Adsorption studies were carried out by varying initial dye concentration, time, and temperature. The activated carbon follows Freundlich adsorption isotherms and it is shown in figure 2. Synthesized carbon follows second-order kinetics and from Van't Hoff equation change in free energy was also calculated and its results were discussed in this chapter.

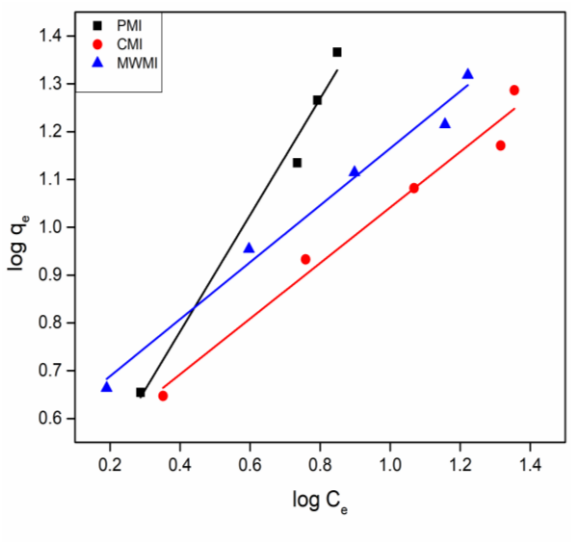

Fig 2: Freundlich adsorption isotherm for synthesized activated carbons on MG dye

Chapter 3B

It deals with the study of the adsorption of oxalic acid on synthesized activated carbons namely, physically modified *Macaranga indica* (PMI), chemically modified *Macaranga indica* (CMI), and microwave-activated *Macaranga indica* leaf MWMI). The adsorption capacities were carried out as a function of contact time, initial concentration, and temperature for studying the isotherm, kinetics, and thermodynamic parameter of the adsorption process. From the study, it is found that activated charcoal follows Langmuir adsorption isotherm, second-order kinetics. Figure 3 depicts the Langmuir isotherm of various synthesized activated carbons.

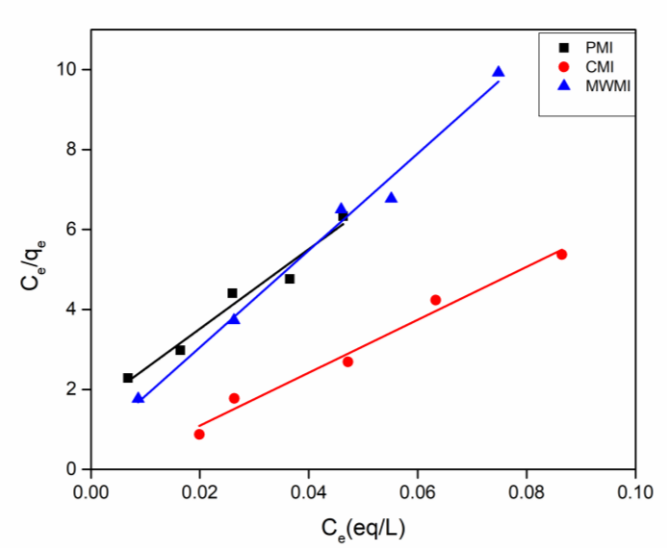

Fig 3: Langmuir adsorption isotherm for synthesized activated carbon

Chapter 4

This chapter describes the adsorption properties of synthesized Java apple leaf carbon. Java apple leaf is an agricultural waste product once it falls from its tree. This was made used for the preparation of activated carbons by three different methods namely physically modified Java apple (PJA), chemically modified Java apple(CJA) and microwave-activated Java apple (MWJA). Further, chapter 4 includes the results of different characterization methods carried out such as P-XRD, FE-SEM, FTIR, and TGA for the analysis of synthesized carbons. The synthesized activated carbon was used for the adsorption of MG and OA and the process of adsorption was studied as a function of initial concentration, contact time, and temperature. From the data, adsorption isotherm, kinetics, and thermodynamics of the adsorption process were analyzed.

Chapter 4A

This includes the discussion of the adsorption of MG dye on various synthesized activated carbon from java apple. Results from the concentration variation indicated that both Langmuir and Freundlich Isotherm models could be used to fit the data. Out of the three synthesized carbons, CJA & MWJA fits for the Freundlich adsorption isotherm where as PJA fits for Langmuir adsorption isotherm. Kinetic studies revealed that the system follows a second-order reaction. Thermodynamic parameters were calculated using Van't Hoff equation and the adsorption process was found to be exothermic and spontaneous. Figure 4 shows the second-order kinetics of the activated carbon.

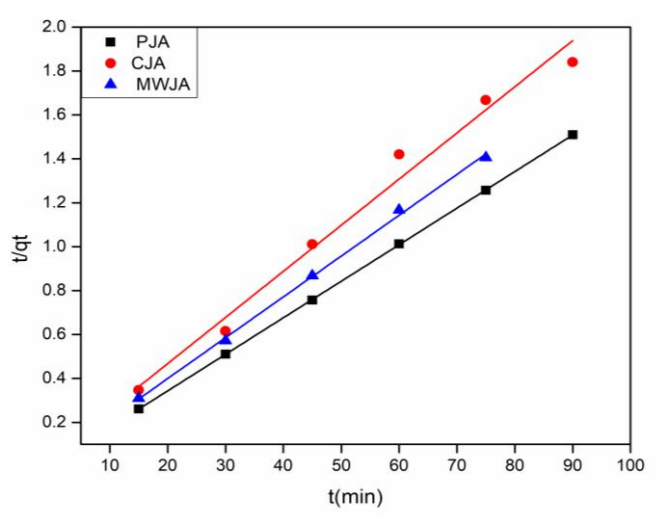

Fig 4: Plot of a second-order kinetic model for the adsorption of MG dye onto PJA, CJA, and MWJA

Chapter 4B

It describes the adsorption study of Java apple leaf on weak acid oxalic acid and adsorption studies were carried out by varying the factors such as initial acid concentration, time, and temperature. It follows the second-order kinetics. Van't Hoff factor was determined by varying temperature. Figure 5 shows the Van't Hoff plot for the synthesized JA leaf carbons with OA.

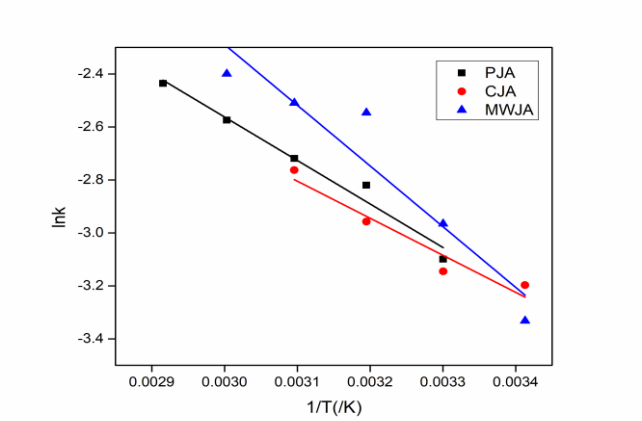

Fig 5: Van't Hoff equation for the adsorption of oxalic acid onto PJA, CJA, and MWJA

Chapter 5

This chapter deals with the preparation and characterization of Cocoa leaf activated carbon and its adsorption behaviour towards Malachite green and oxalic acid. The preparation of activated carbon was carried out by physical, chemical and microwave activation and the resulting carbons were characterized by P-XRD, FE-SEM, FTIR spectroscopy, and TGA techniques. The adsorption process is described in terms of adsorption isotherm, kinetics and thermodynamics of adsorption.

Chapter 5A

This chapter discusses with characterization and adsorption study of synthesized activated carbon with MG dye. The activated carbons were used for the adsorption of MG dye by varying the factors such as contact time, initial dye concentration, and temperature. The adsorption data were studied by Freundlich and Langmuir adsorption isotherm, rate of adsorption was determined by studying first and second-order kinetic models. Thermodynamic parameters such as ΔH, ΔG, and ΔS were calculated by varying the temperature. As temperature increases the amount of dye adsorption also increases and that is shown in the figure 6.

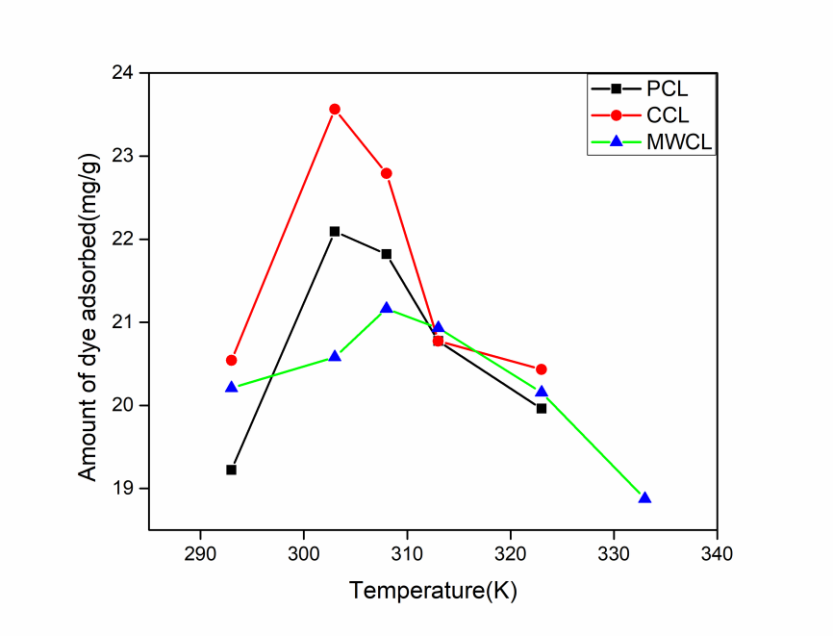

Fig.6 Effect of temperature on the adsorption of MG on PCL, CCL, and MWCL

Chapter 5B

It deals with the study of the adsorption of oxalic acid onto synthesized activated carbon. A comparison study of three synthesized carbons with OA is discussed in this particular chapter. Enthalpy changes, change in entropy, and change in free energy were calculated by varying the temperature. Figure 7 gives the plot Van't Hoff equation for the adsorption of oxalic acid on all three synthesized carbons.

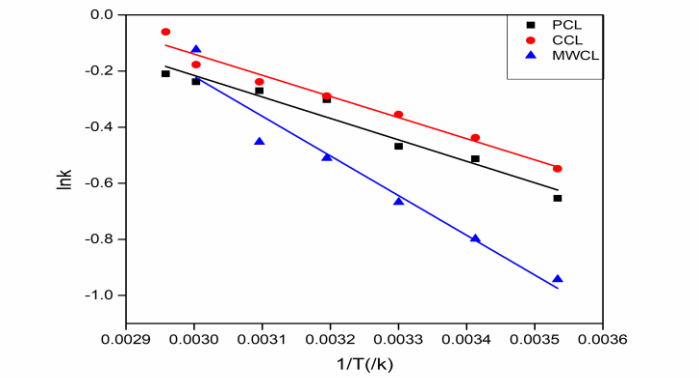

Fig.7 Van't Hoff equation for the adsorption of OA onto PCL, CCL, and MWCL

Chapter 6

This chapter includes the comparison study of the efficiency of adsorption of various synthesized carbons by MG dye and OA and also the conclusion of the research work.

In the present study, different activated carbons were derived from the raw materials, namely, *Macaranga indica*, java apple, and cocoa leaves. The activated carbons were obtained by three different methods, namely, physical, chemical, and microwave activation. The porosity and the number of active centres also differ as the preparation conditions are changed. The resulting activated carbons were found to show different surface properties and hence different adsorption capacities toward dye and acid. The comparison between the surface property and adsorption efficiencies of synthesized activated carbons towards the adsorption of Malachite green and oxalic acid is discussed here.

This chapter also includes the comparison of synthesized activated carbon with commercial charcoal and it can be found that the commercial activated charcoal shows higher adsorption capacity than the synthesized activated carbon under the studied conditions. Even though the efficiency is more, the use of commercial activated charcoal needs to be restricted due to its high cost.

It includes the conclusion of the research work. Commercial activated carbon, which is obtained from coal and animal-based materials, is expensive and this restricts the large-scale use of commercial activated carbon in various fields. Hence activated carbon derived from agricultural waste materials is expected to be a good replacement for commercial charcoal. The raw materials selected for the preparation of such activated carbon are agricultural waste materials which are available in plenty. The advantages of using such waste materials for the preparation of activated carbon are definitely of lower cost activated carbons and at the same time, the number of agricultural waste materials spread on the land will be reduced. These carbons are found to have good adsorption properties.

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1. **Sneha, B.S.,** Narayana, B. and Ishwara, Bhat, J., Adsorption of Malachite Green Dye using Low Cost Adsorbent derived from Java Apple Leaves (Syzyium samarangense): Kinetic and Thermodynamic Study., *Sadhana –springer (http;/doi.org/*10.1007/s12046-023-02214-z).

2. **Sneha, B. S.,** and Ishwara, Bhat, J., Importance of Synthesized Activated Carbon as an Adsorbent on Oxalic Acid., Recent Advances in Materials Science and Biophysics (2018): P179.-182. (ISBN: 978-93-5291-953-6)

3. **Sneha, B.S** and Ishwara, Bhat, J., Importance of Activated carbon as an adsorbent on Oxalic Acid: A kinetic and Thermodynamic study Proceedings of NCASEM(2019): P 362-365. (ISBN: 978-81-934215-3-6)

4. **Sneha, B.S.,** and Narayana, B., Characterization and Adsorption Studies of Macaranga indica Activated carbon communicated in Indian Journal of Science and Technology.
5. **Sneha, B.S.,** and Ishwara, Bhat, J., Synthesis and characterization of Activated carbon as an adsorbent on malachite green dye., presented at in 37^{th} Annual National Conference of Indian Council of Chemists held during 12^{th} -14^{th} December 2018 held at NITK, Surathkal, Mangalore, Karnataka.

6. **Sneha, B.S** and Ishwara, Bhat, J., Adsorption of Malachite green dye on activated carbons of Java Apple leaves presented a paper in International Conference on Advanced Functional Materials for Energy, Environment and Health Care (AFMEEHC) held during 18^{th} - 20^{th} March 2019 held at University of Mysore, Mysore.
7. **Sneha, B.S** and Narayana, B., Comparative study of Adsorption of Malachite Green Dye and Oxalic acid Using Low-Cost Adsorbent derived from Cocoa Leaves: Kinetic and Thermodynamic Study presented in International conference on Functional Materials for Advanced Technolgies-1 (ICFMAT 1) held during 2-4^{th} January 2023 organized by the department of physics, Central University of Kerala.

Professor B. Narayana **Sneha B.S.**

(Research Guide) **(Research Student)**